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EP-A- 0 054 942  
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CHEMICAL PATENTS INDEX - BASIC AB-  
STRACTS JOURNAL, Section A, Week 8805,  
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## Description

The present invention relates to adhesives for metals, especially precious metals, particularly for use in dentistry. The term "adhesive" used in the present specification includes primers used when a metallic material is bonded to other materials.

Adhesives composed of polymerizable monomers such as acrylic monomers and epoxy compounds are in general used to bond metallic materials because of their good workability and their ability to cure in a short time at normal temperature under normal pressure. However, they suffer from the serious disadvantage in some applications where water resistance is required, because their bond strength rapidly decreases when the bonding interface is permanently exposed to water.

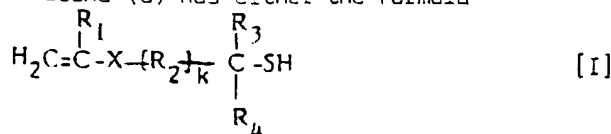
In the field of dental materials, attempts have recently been made to obtain a polymerization-curing adhesive having a high bond strength for metals and good water resistance. These attempts are bearing fruit. An example is a dental adhesive incorporated with an organophosphate ester, as disclosed in U.S. Patent US-A-4,539,382. It produces a high bond strength that is very little affected by water when applied to base metals such as iron, nickel, chromium, cobalt, tin, aluminum, copper, and titanium, and their alloys, and it is now in practical use as a dental adhesive. Unfortunately, when it is used for dental casting (e.g., inlay, crown, and bridge) of precious metal alloys (e.g., gold, platinum, palladium and silver alloys), the bond strength is more affected by water than when it is used for base metal alloys. To keep the bond strength unaffected by water, it was necessary that the adherend of precious metal alloys undergo surface treatment such as tin plating or oxidation.

In the journal of the Japanese Society for Dental Materials and Devices, vol. 5, p. 92-105 (1986), it was reported that the bond strength for precious metals becomes moderately unaffected by water when an MMA-tributyl borane adhesive is applied to a precious metal adherend primed with N-(4-mercaptophenyl)-methacrylamide.

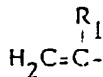
Adhesives containing N-(4-mercaptophenyl)methacrylamide, unlike those disclosed in US-A-4,539,382, do not need surface treatment of the adherend. However, they are not practically satisfactory in that the bond strength is affected by water.

The present invention provides an adhesive comprising (a) an olefinically unsaturated compound having at least one mercapto group or polysulfide group joined to a saturated carbon atom and (b) either a solvent that does not copolymerize with the said compound, or a liquid polymerizable monomer that does copolymerize with the said compound.

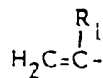
Compound (a) has either the formula



where R<sub>1</sub> is a hydrogen atom or methyl group; R<sub>2</sub> is a C<sub>1-10</sub> organic group (which may contain a



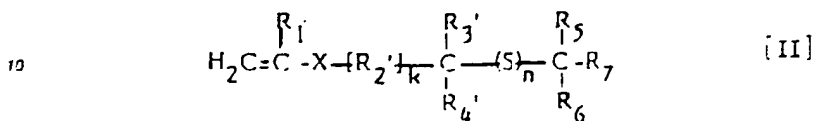
group and/or mercapto group); each of R<sub>3</sub> and R<sub>4</sub> is a C<sub>1-40</sub> organic group (which may contain a



group and/or mercapto group), a hydrogen or halogen atom, or a mercapto group; or two or three of R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are optionally joined to each other to form a cyclic structure when R<sub>3</sub> and/or R<sub>4</sub> is an organic group; X denotes -COO-, -OOC-, -CONH-, -COS-, -SOC-, -S-, or



5 and k is 0 or 1, or the formula



15 where  $\text{R}_1$ , k and X are as defined above;  $\text{R}_2'$  is a  $\text{C}_1$ - $\text{C}_6$  organic group (which may contain a



group and/or polysulfide group); each of  $\text{R}_3'$ ,  $\text{R}_4'$ ,  $\text{R}_5$ ,  $\text{R}_6$  and  $\text{R}_7$  is a  $\text{C}_1$ - $\text{C}_6$  organic group (which may contain a



30 group and/or polysulfide group), a hydrogen or halogen atom, or a mercapto group; or two or three of  $\text{R}_2'$ ,  $\text{R}_3'$ , and  $\text{R}_4'$  are optionally joined to each other to form a cyclic structure when  $\text{R}_3'$  and/or  $\text{R}_4'$  is an organic group; and/or two or three of  $\text{R}_5$ ,  $\text{R}_6$ , and  $\text{R}_7$  are optionally joined to each other to form a cyclic structure when they are organic groups; and n denotes an integer of from 2 to 6.

Such adhesives or primers can be used to treat the adherend surface prior to bonding to ensure firm bonding between a metal (especially precious metal) object and a metal or non-metal object, and to bond a metal (especially precious metal) object to a metal object or non-metal object.

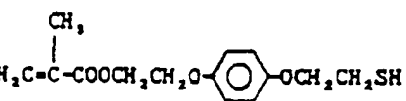
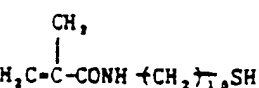
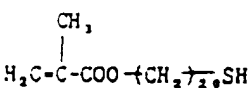
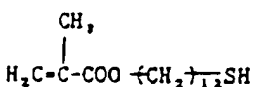
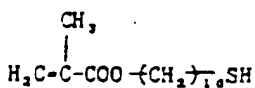
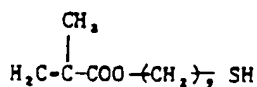
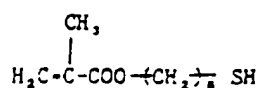
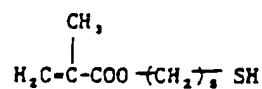
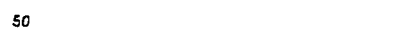
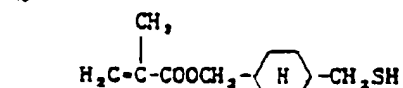
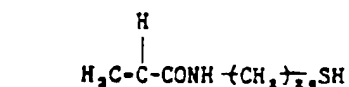
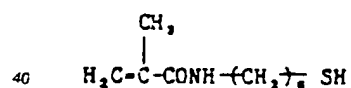
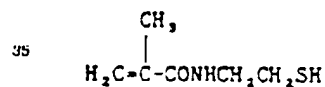
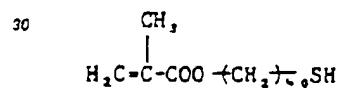
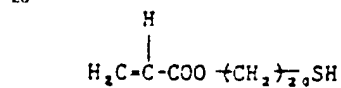
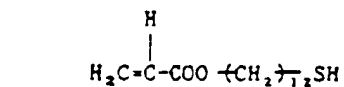
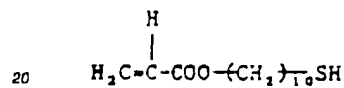
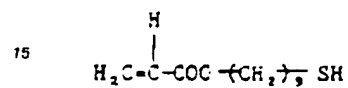
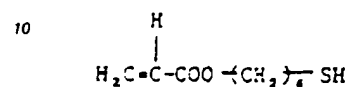
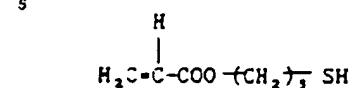
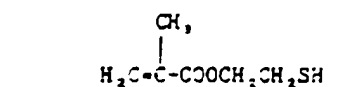
Examples of the compound (a) are given below.

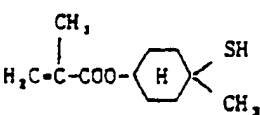
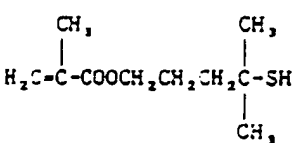
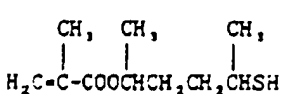
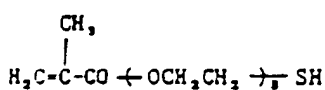
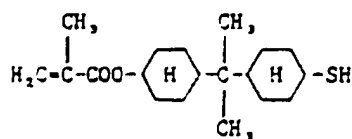
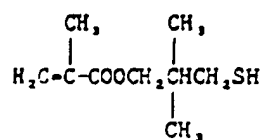
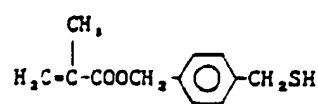
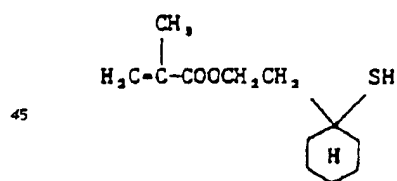
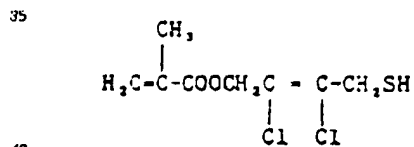
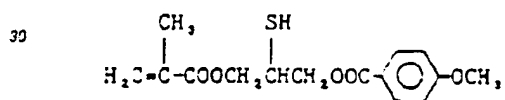
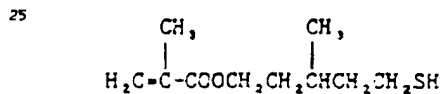
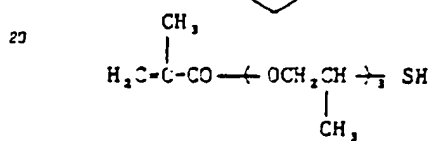
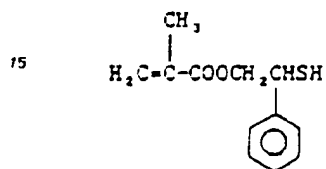
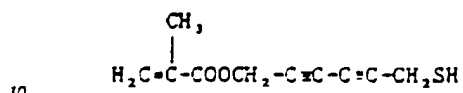
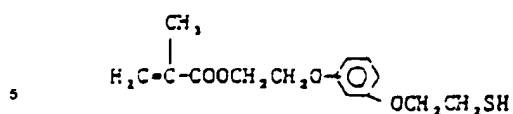
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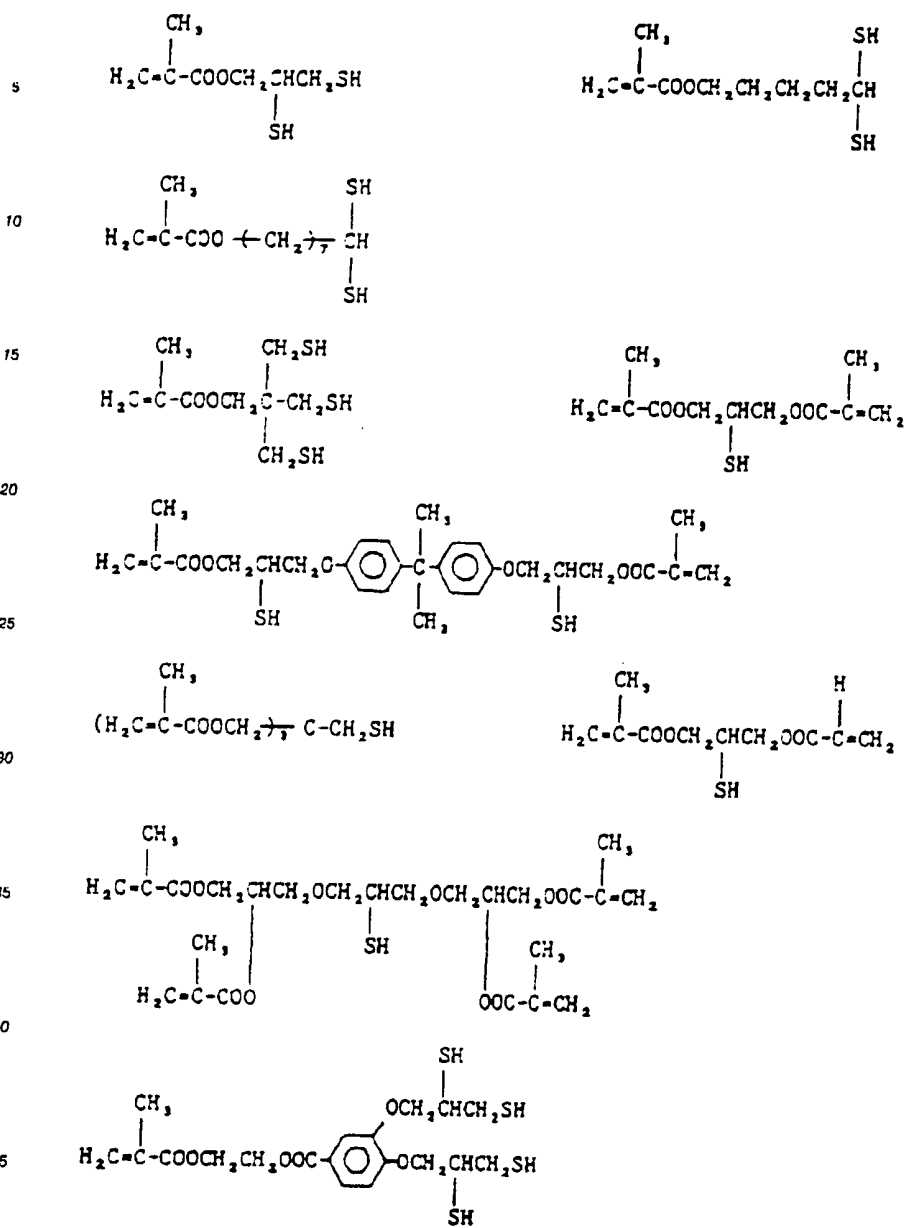
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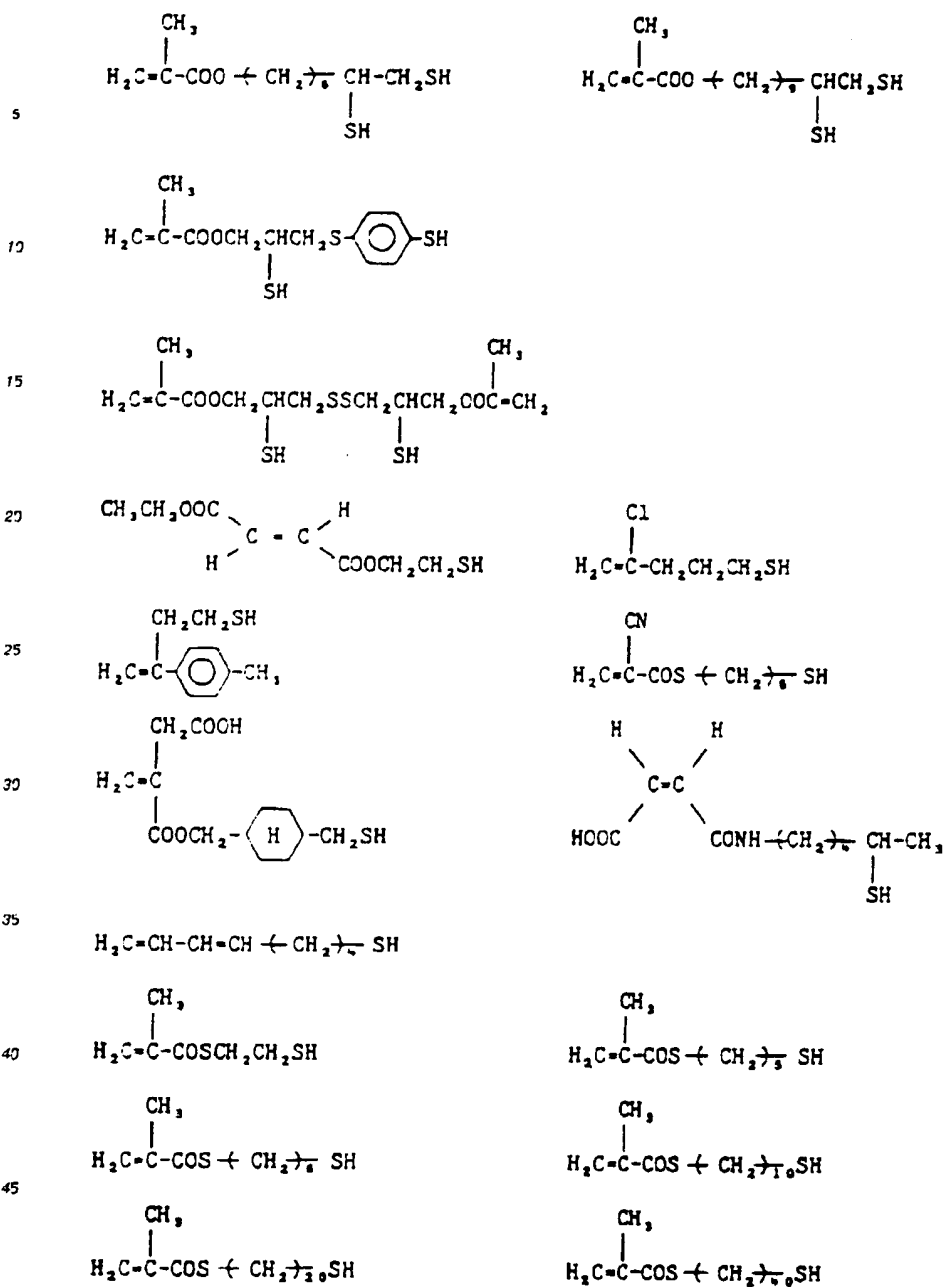
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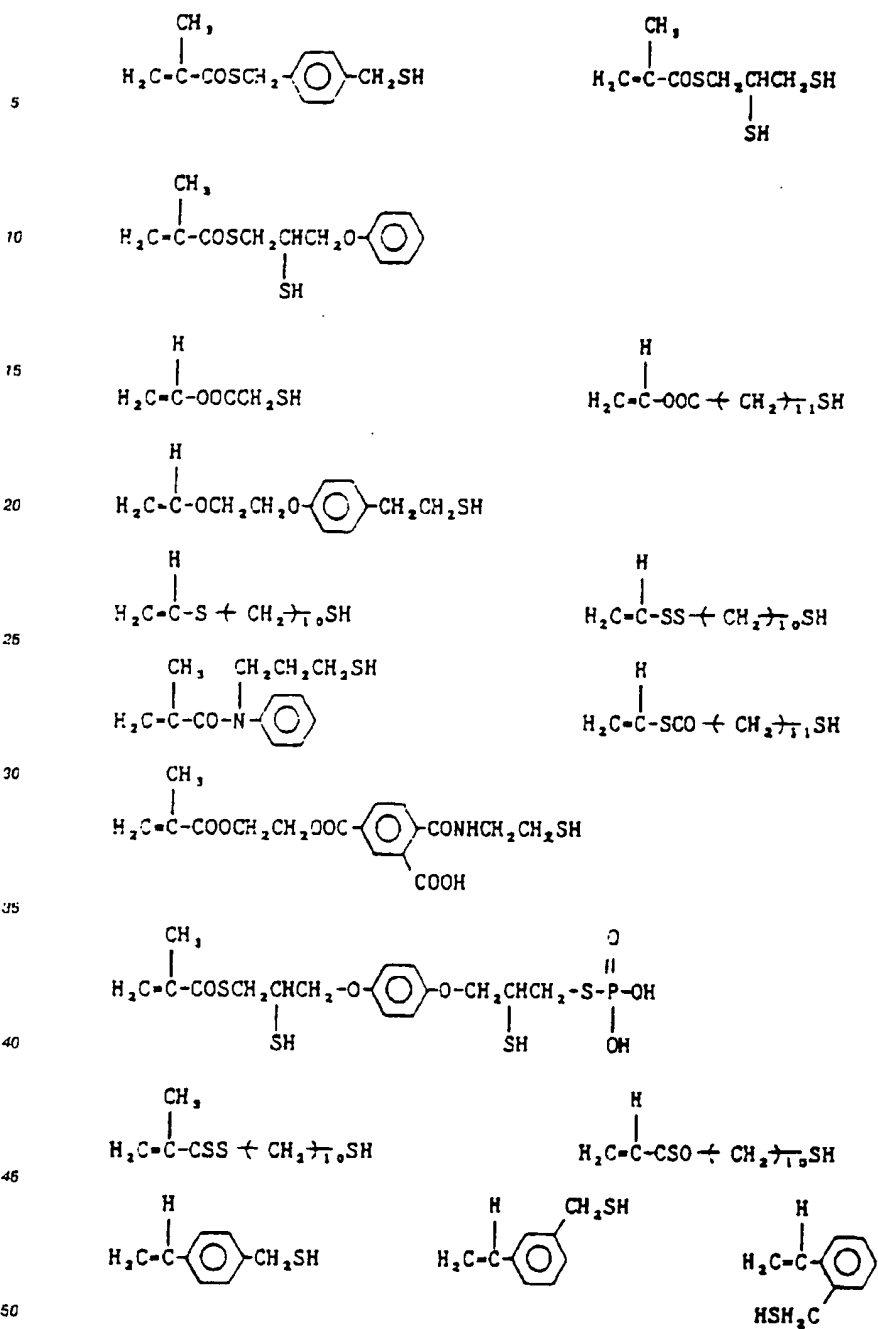
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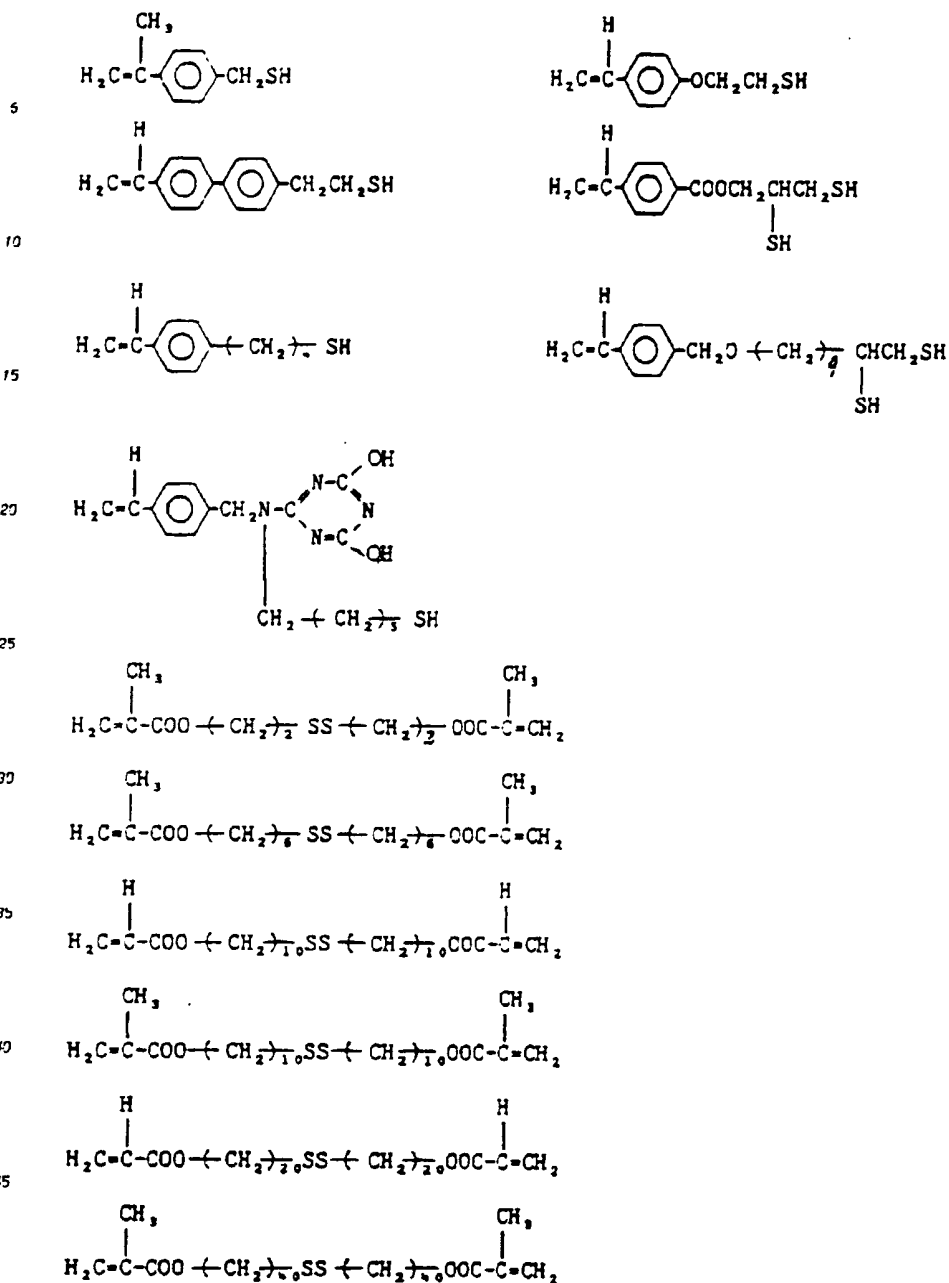


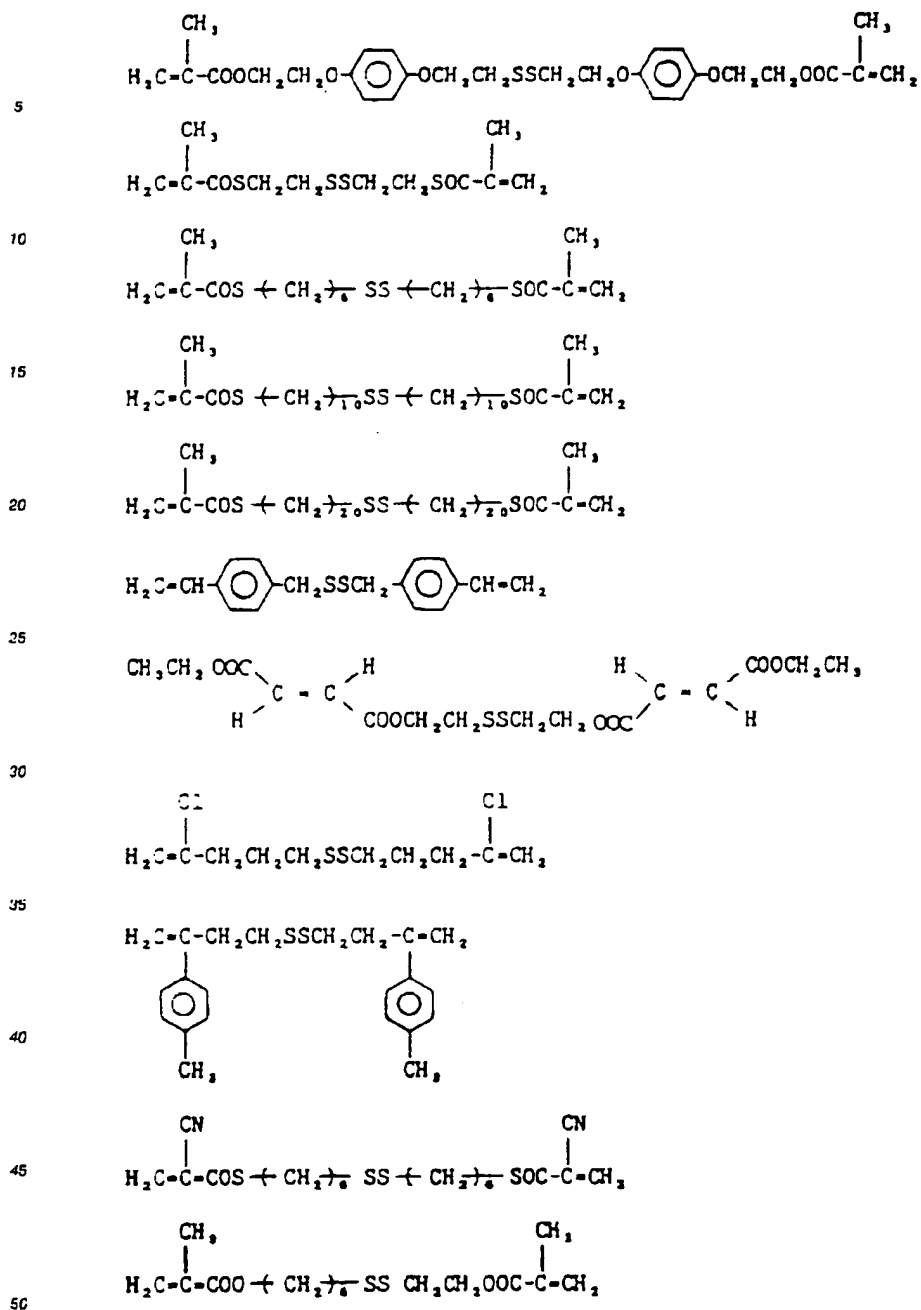




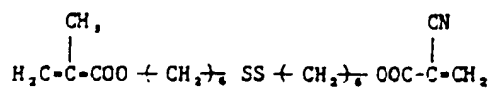




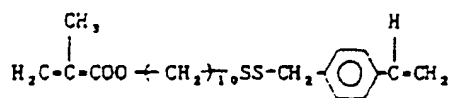




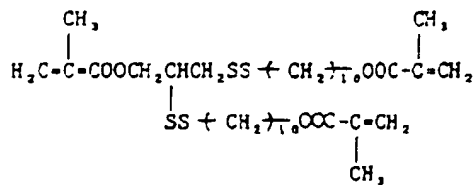
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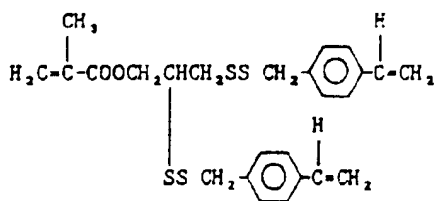
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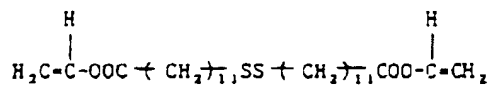


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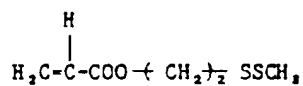


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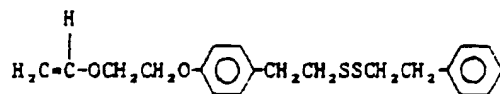
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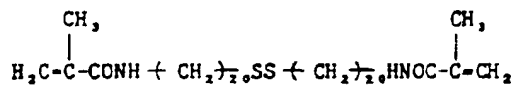
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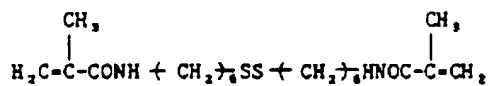
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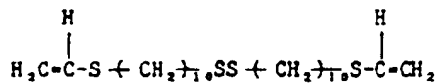
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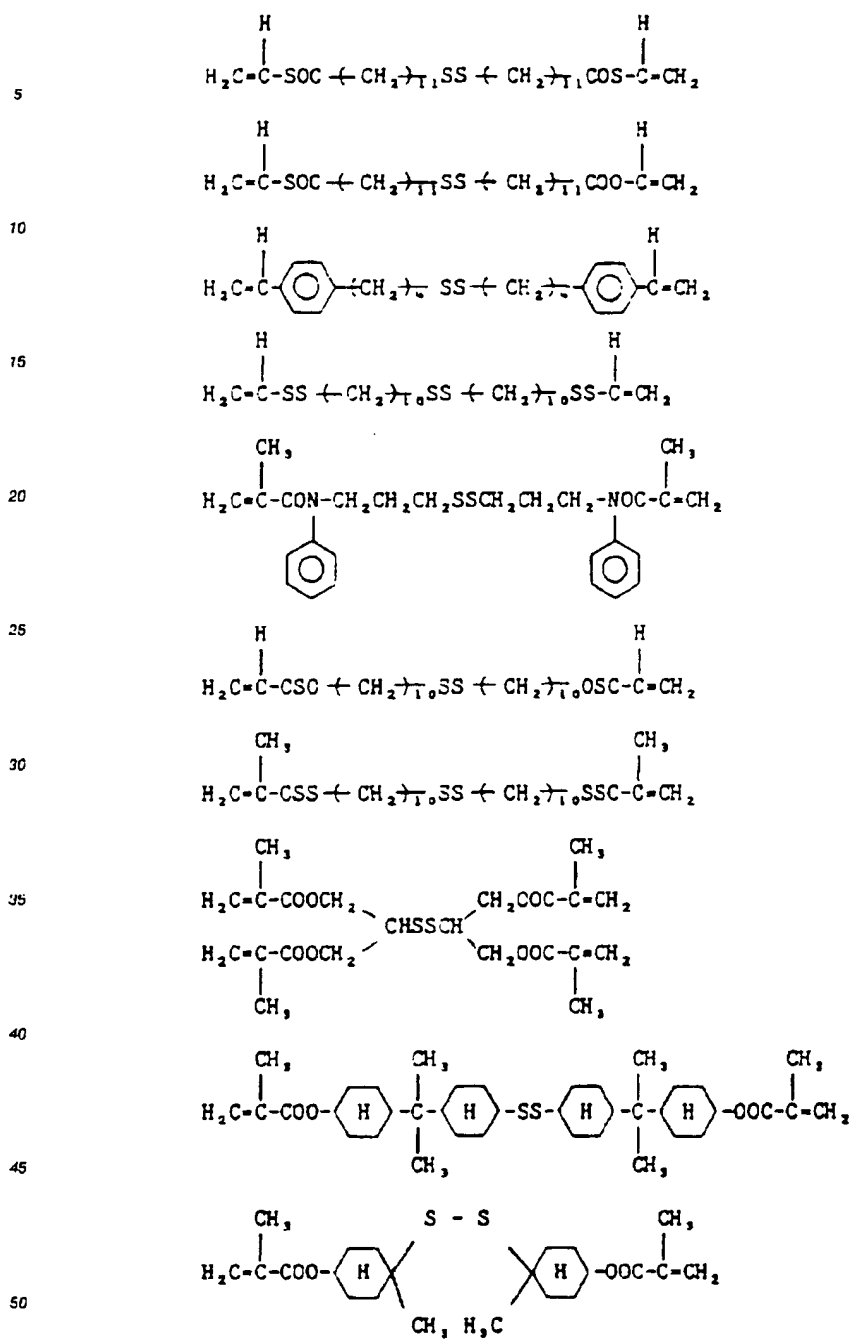


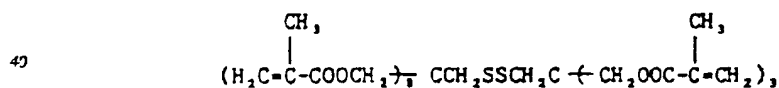
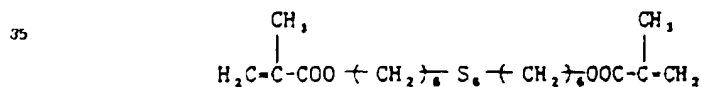
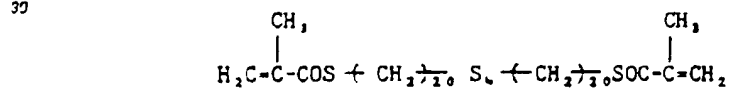
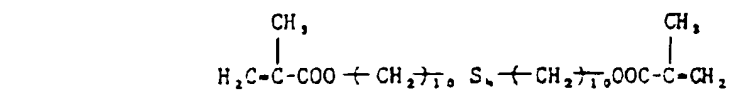
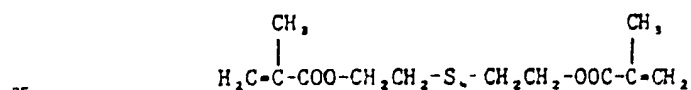
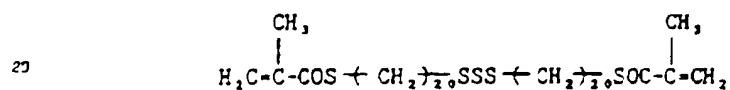
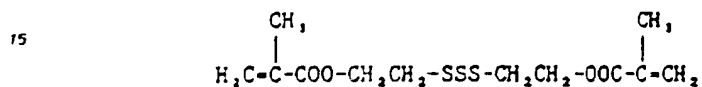
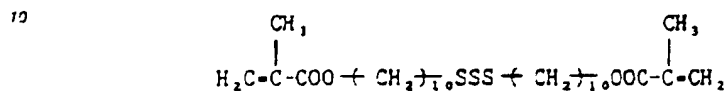
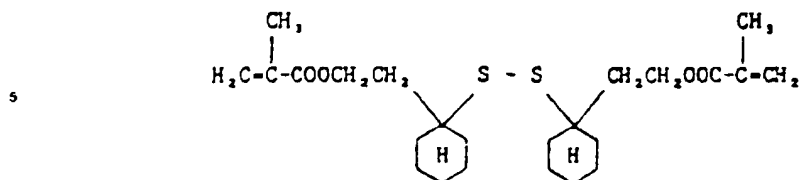
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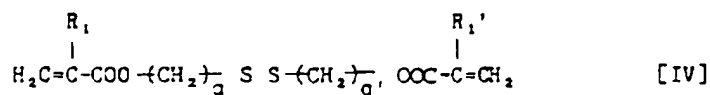




Among the compounds represented by the formulas [I] and [II] above, the compounds represented by the formulas [III] and [IV] are especially practical.



where R<sub>1</sub> is as defined above; and m denotes an integer of 6 to 20.



where  $R_1$  is as defined above;  $R_1'$  is the same as  $R_1$ ; and  $q$  and  $q'$  each denote an integer of 2 to 20.

The above-mentioned compound (a) used as an adhesive component in the present invention can be synthesized according to the process described in "Shin-Jikken Kagaku Koza", Vol. 14, (published by Maruzen, 1977-8), The Chemistry of the Thiol Group (published by John Wiley & Sons, 1974), and Comprehensive Organic Chemistry, Vol. 3 (published by Pergamon Press, 1979).

For example, the compound represented by the formula [I] can be synthesized through any of the following three routes.

(1) Synthesis starts from a compound of the same chemical structure as represented by the formula [I] which has a hydroxyl group, amino group, or halogen atom in place of the mercapto group. The compound of the formula [I] is obtained by replacing the hydroxyl group, amino group, or halogen atom by a mercapto group.

(2) By the codensation of (meth)acrylic acid chloride or (meth)acrylic acid anhydride with a compound represented by the formula [V] below.



where  $R_2$ ,  $R_3$ ,  $R_4$ , and  $l$  are as defined in the formula [I]; and  $Y$  denotes a mercapto group, hydroxyl group, or amino group.

(3) By the reductive cleavage of the disulfide linkage in a compound represented by the formula [II] in which  $n$  is 2.

Incidentally, when the process (1) is applied in the usual way to a compound having an olefinic double bond with a substituent electron attracting group, it is difficult to obtain a compound represented by the formula [I] because the mercaptide ion represented by the formula [VI] below, which occurs as an intermediate, extremely readily attaches to the double bond.



This difficulty can be effectively avoided by adding a large excess of heavy metal ions (such as  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Ag^+$ , and  $Hg^{2+}$ ) to the reaction system so that the mercaptide ion [VI] formed is removed and recovered in the form of insoluble metal salt from the reaction system and subsequently treating the metal salt with a strong acid such as hydrochloric acid to liberate the compound of the formula [I].

The compound represented by the formula [II] can be synthesized through either of the following two routes.

(1) By preparing a thiol compound [I] having an olefinic double bond and subsequently changing this compound into a polysulfide by condensation.

(2) By introducing an olefinic double bond into a compound having the polysulfide linkage.

The adhesive of the present invention is prepared from the above-mentioned compound (a) by the following process (1) or (2).

(1) The compound (a) is dissolved in a solvent to give the adhesive. The solvent is a volatile organic solvent having a boiling point lower than  $250^\circ C$  (e.g., methanol, ethanol, 2-ethyl butanol, acetone, methyl ethyl ketone, diethyl ketone, ethyl ether, n-butyl ether, 1,4-dioxane, tetrahydrofuran, ethyl acetate, toluene, xylene, hexane, octane, methylene chloride, 1,2-dichloroethane, and 1,1,2,2-tetrachloroethane),

or water, or a mixture thereof. The concentration of the above-mentioned compound is 0.0001 to 99 wt% (preferably 0.001 to 50 wt%) based on the total amount of the compound and the solvent. To the solution is added a polymerization initiator and copolymerizable monomer (mentioned later), according to need.

The thus obtained adhesive is applied as a primer to the surface of a metal adherend, and subsequently an adhesive or a composite resin used in the usual way is applied to the primer coat to bond the metal adherend to another metal adherend or non-metal adherend.

(2) The compound (a) is dissolved in a monomer which copolymerizes with it to give the adhesive. The copolymerizable monomer is explained later. The concentration of the compound (a) is 0.005 to 99 wt% based on the total amount of the compound and the copolymerizable monomer. To the solution is added a filler and polymerization initiator, according to need. The adhesive of the present invention can also be obtained by adding the compound (a) to a commonly used adhesive (which is composed of a polymerizable monomer and a polymerization initiator and which may contain a filler). In this case, the concentration of the compound (a) should be 0.005 to 99 wt% (based on the total amount of the compound (a) and the copolymerizable monomer).

In the case of (1) above, the compound (a) exhibits the adhesion promoting effect even when its amount is very small, because the effect is attributable to the monomolecular layer formed on the adherend surface by adsorption. This adhesion promoting effect remains even when the primer coat is washed with a solvent.

The adhesive of the present invention is used preferably as a primer. To the primer coat is applied a known adhesive of polymerization curing type, preferably an adhesive containing an acrylic monomer, as mentioned above. The tensile bond strength thus achieved is usually higher than 200 kg/cm<sup>2</sup>, depending on the mechanical strength of the adhesive per se. Almost all failure is cohesive failure or adherend failure. The bond interface has such an extremely good water resistance that the bond strength does not decrease appreciably when the adherend is dipped in water at normal temperature for several months.

The copolymerizable monomer used for the adhesive (especially that mentioned in (2) above) of the present invention should preferably be a (meth)acrylic ester such as methyl methacrylate, 2-hydroxyethyl methacrylate, ethylene glycol dimethacrylate, triethylene glycol dimethacrylate, neopentyl glycol dimethacrylate, 2,2-bis[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane (called Bis-GMA), 2,2-bis-[methacryloyloxyethoxyphenyl]propane, trimethylethane triacrylate, pentaerythritol tetraacrylate, 4-(2-methacryloyloxyethyl) trimellitate, 4-methacryloyloxyethyl trimellitate anhydride, bis(2-methacryloyloxyethyl) hydrogen phosphate, 2-methacryloyloxyethylphenyl hydrogen phosphate, 6-methacryloyloxyhexyl dihydrogen phosphate, 10-methacryloyloxydecyl dihydrogen phosphate, tris(2-methacryloyloxyethyl) phosphate, and N,N-dimethylaminoethyl methacrylate.

The adhesive of the present invention is usually incorporated with a polymerization initiator as mentioned above. It includes benzoyl peroxide-aromatic tertiary amine, peroxide (cumene hydroperoxide, etc.), tributyl borane, and aromatic sulfinic acid (or salt thereof)-aromatic secondary or tertiary amine-acyl peroxide. It further includes photopolymerization initiators such as camphorquinone, camphorquinone-tertiary amine, camphorquinone-aldehyde, and camphorquinone-mercaptan.

In the case where the adhesive of the present invention is used as a primer and another adhesive is applied onto the primer coat, it is not necessary that the adhesive of the present invention contains a polymerization initiator. In such a case, a polymerization initiator in the adhesive migrates into the primer coat to effect polymerization curing of the primer.

The adhesive of the present invention may be incorporated with an inorganic filler such as quartz, glass, hydroxyapatite, calcium carbonate, barium sulfate, titanium oxide, and zirconium oxide; and polymer powder such as poly(methyl methacrylate), polystyrene, and polyvinyl chloride.

The adhesive of the present invention may be applied to precious metals such as gold, platinum, palladium, silver, ruthenium, rhodium, osmium, and iridium; and base metals such as iron, nickel, cobalt, copper, zinc, tin, aluminum, titanium, vanadium, chromium, manganese, zirconium, molybdenum, cadmium, and antimony. It also exhibits the adhesion promoting effect when applied to metal oxides such as aluminum oxide, titanium oxide, and zirconium oxide, and ceramics containing such metal oxides.

Since the adhesive of the present invention provides a high bond strength which is very little affected by water when applied to precious metals, it can be suitably used in the field of dentistry. For example, it is used to bond a precious metal casting such as inlay, crown, and bridge to a tooth. It is also used to prepare a prosthetic appliance of precious metal by bonding a pontic to a bridge frame-work or bonding separately cast parts together. The bonding will provides improved performance and workability which were not achieved with the conventional technique. The adhesive of the present invention can be used not only in the field of dentistry but also in any industrial field where the bonding of metals and metal oxides is necessary.

The invention will be understood more readily by reference to the following examples; however, these examples are intended to illustrate the invention and are not to be construed to limit the scope of the

invention.

(Production of thiol compound)

#### 5 Production Example 1

In a 500-cc three-neck flask was placed 50 g of a mixture composed of 10-hydroxydecyl methacrylate (59%) and 1,10-dimethacryloyloxy decane (41%), and the flask was cooled in an ice bath. 30 g of p-toluene-sulfonyl chloride dissolved in 80 cc of pyridine was slowly added dropwise with stirring through a dropping funnel connected to the flask. The reaction temperature was kept at 0°C for 2 hours, and then raised to room temperature. Stirring was continued for 2 hours, and the reaction product was neutralized with 6N HCl. The liberated organic substance was extracted with methylene chloride, followed by washing with water several times and drying with anhydrous magnesium sulfate. After the addition of 0.1 g of hydroquinone monomethyl ether, the methylene chloride was evaporated away at a temperature below 40°C under reduced pressure. Thus there was obtained 79 g of a mixture composed of p-toluenesulfonate of 10-hydroxydecyl methacrylate and 1,10-dimethacryloyloxy decane.

This mixture together with 11 g of thiourea and 0.4 g of 2,2'-methylenebis(4-ethyl-6-tert-butylphenol) were dissolved in 150 cc of ethanol. The solution was refluxed for 30 minutes and then ethanol was evaporated away under reduced pressure. The residues were extracted with acetonitrile and acetonitrile was evaporated away under reduced pressure from the extract. Thus there was obtained a crude isothiuronium salt. It was washed with a large amount of n-hexane to remove 1,10-dimethacryloyloxy decane. Thus there was obtained a isothiuronium salt of high purity.

In methanol were dissolved 48 g of the isothiuronium salt and 40 g of zinc chloride. With vigorous agitation, a methanol solution of sodium hydroxide was added dropwise to form a white precipitate of zinc salt of 10-mercaptodecyl methacrylate. The addition was continued until no precipitate appeared any longer. The salt was filtered out and washed with water, followed by drying. The amount of the salt obtained was 31 g. To 20 g of this salt was added 200 ml of methanol to give a suspension. Upon addition of dilute hydrochloric acid, the salt dissolved to liberate 10-mercaptodecyl methacrylate. This compound was extracted with n-hexane, the extract was dried with anhydrous magnesium sulfate, and n-hexane was evaporated away under reduced pressure. Thus, there was obtained 12 g of 10-mercaptodecyl methacrylate in the form of colorless transparent liquid.

This compound was analyzed by NMR (90 MHz, 10% CDCl<sub>3</sub> solution, at room temperature). The following NMR data was obtained.

$\delta$  = 5.35-5.00 5.90-6.05 : ethylenic protons of methacryloyl group  
 $\delta$  = 1.75-1.85 : methyl protons of methacryloyl group  
 $\delta$  = 3.90-4.10 : protons of methylene adjacent to an oxygen atom  
 $\delta$  = 2.15-2.60 : protons of methylene adjacent to a sulfur atom  
 $\delta$  = 0.8-1.7 : remaining methyl protons and proton of mercapto group

Mass spectroscopic analysis gave a molecular ion peak at m/e 258. Thus the compound was identified as 10-mercaptodecyl methacrylate.

(Production of disulfide compound)

#### Production Example 2

In 200 ml of ethanol was dissolved 10 g of 10-mercaptodecyl methacrylate. To the solution was added dropwise, with vigorous stirring, an ethanol solution of iodine until the color of iodine did not disappear any longer. Ethanol was evaporated away. To the residue was added 200 ml of methanol and the organic compound was extracted with hexane. Hexane was evaporated away. The major component of the residue was isolated by column chromatography (Wakogel C-200 (made by Wako Pure Chemical Industries, Ltd.) and hexane-ethyl acetate as an eluent). There was obtained 6.2 g of colorless transparent liquid.

This compound was analyzed by liquid chromatography. The chromatogram gave no peak of 10-mercaptodecyl methacrylate as the starting material, but gave a major peak (95.5%) at other elution time.

This compound was also analyzed by NMR (90 MHz, 10% CDCl<sub>3</sub> solution, at room temperature). The following NMR data was obtained.

$\delta$  = 5.00-5.35 5.90-6.05 : ethylenic protons of methacryloyl group  
 $\delta$  = 1.75-1.85 : methyl protons of methacryloyl group  
 $\delta$  = 3.90-4.10 : protons of methylene adjacent to an oxygen atom



$\delta = 2.15-2.60$  : protons of methylene adjacent to a sulfur atom

$\delta = 0.8-1.7$  : remaining methyl protons

Thus the compound was identified as bis(10-methacryloyloxydecyl)-disulfide.

5 (Adhesive)

Examples 1 to 13 and Comparative Examples 1 and 2

Thirteen compounds shown in Table 1 and the above-mentioned known compound N-(4-mercap-  
10 tophenyl)methacrylamide were examined for adhesion to previous metals in the following manner.

Each compound was dissolved in acetone to give a 1 wt% primer. The primer was applied by brushing  
to the following three adherends.

- 1) A pure gold plate, measuring 10 x 10 x 1 mm, polished with silicon carbide abrasive paper (1000 grit)  
and backed with a 4-mm thick stainless steel plate.
- 15 2) "Cast Well" of dental gold-silver-palladium alloy, measuring 10 x 10 x 1 mm, (made by G-C Dental  
Industrial Corp.) backed with a 4-mm thick stainless steel plate.
- 3) "Degudent Universal" of dental gold-platinum-palladium alloy, measuring 10 x 10 x 1 mm, (made by  
Mitsubishi Metal Corp.) backed with a 4-mm thick stainless steel plate.

One minute after application, the coating was washed with pure acetone so that only the molecules  
20 adsorbed on the surface remain. The washed coating was covered with a piece of adhesive tape having a  
hole 5 mm in diameter. The primer-coated surface exposed through the hole serves as an adherend.

On the other hand, a round rod of SUS304, measuring 7 mm in diameter and 25 mm long, was  
provided. The end of the rod was roughed by sand blasting with 50- $\mu$ m alumina abrasive grains. On the  
roughed end was placed "Panavia EX" paste (a dental adhesive made by Kuraray Co., Ltd.) composed of  
25 100 parts by weight of methacrylate ester, 3 parts by weight of sodium sulfinate-benzoyl peroxide-tertiary  
amine polymerization initiator, and 320 parts by weight of silane-treated inorganic filler. The rod end was  
pressed against the adherend to effect adhesion. One hour later, the bonded test pieces were immersed in  
water at 37°C for 24 hours. After water immersion, the tensile bond strength was measured using a  
universal tester (made by Instron Ltd.) at a cross-head speed of 2 mm/min. An average of measurements of  
30 eight samples were obtained. The results are shown in Table 1.

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Table 1

Example No.	Primer compound	Adhesion to pure gold (kg/cm <sup>2</sup> )	Adhesion to Cast Well (kg/cm <sup>2</sup> )	Adhesion to Degudent Universal (kg/cm <sup>2</sup> )
1	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}-\text{C}-\text{COSCH}_2\text{CH}_2\text{SH} \end{array}$	252	266	301
2	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}-\text{C}-\text{COO}-(\text{CH}_2)_3\text{SH} \end{array}$	292	318	343
3	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}-\text{C}-\text{COO}-(\text{CH}_2)_6\text{SH} \end{array}$	327	341	349
4	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}-\text{C}-\text{COS}-(\text{CH}_2)_8\text{SH} \end{array}$	301	325	337
5	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}-\text{C}-\text{COO}-(\text{CH}_2)_{11}\text{SH} \end{array}$	348	356	374
6	$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}-\text{C}-\text{COO}-(\text{CH}_2)_3\text{SH} \end{array}$	352	348	392
7	$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}-\text{C}-\text{CONH}-(\text{CH}_2)_8\text{SH} \end{array}$	350	341	377
8	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}-\text{C}-\text{COOCH}_2\text{CH}_2\text{O}-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}_2\text{SH} \end{array}$	353	347	381

5	9	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{COO}-\left(\text{CH}_2\right)_6-\text{CHCH}_2\text{SH} \\   \\ \text{SH} \end{array}$	365	359	388
10	10	$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C}-\text{S}-\left(\text{CH}_2\right)_{10}-\text{SH} \end{array}$	315	333	339
15	11	$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C}-\text{OCO}-\left(\text{CH}_2\right)_{11}-\text{SH} \end{array}$	305	296	314
20	12	$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C}-\text{SCO}-\left(\text{CH}_2\right)_{11}-\text{SH} \end{array}$	326	343	324
25	13	$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C}-\text{C}_6\text{H}_4-\left(\text{CH}_2\right)_6-\text{SH} \end{array}$	341	330	376
30	Comparative Example 1	N-(4-mercaptophenyl)-methacrylamide	234	243	173
35	Comparative Example 2	None	171	151	128

Examples 14 to 27

Fourteen compounds as shown in Table 2 were examined for adhesion to pure gold plate and "Degudent Universal" in the same manner as in Examples 1 to 13. The results are shown in Table 2.

Table 2

Example No.	Primer compound	Adh sion to pure gold (kg/cm <sup>2</sup> )	Adh sion to Degudent Universal (kg/cm <sup>2</sup> )
14	$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C}-\text{CCC}-(\text{CH}_2)_2-\text{SSCH}_3 \end{array}$	243	274
15	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{COO}-(\text{CH}_2)_7-\text{SS}-(\text{CH}_2)_2-\text{OOC}-\text{C}=\text{CH}_2 \\   \\ \text{CH}_3 \end{array}$	257	288
16	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{COSCH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{SOC}-\text{C}=\text{CH}_2 \\   \\ \text{CH}_3 \end{array}$	248	276
17	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{COS}-(\text{CH}_2)_6-\text{SS}-(\text{CH}_2)_6-\text{SOC}-\text{C}=\text{CH}_2 \\   \\ \text{CH}_3 \end{array}$	312	330
18	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{COG}-(\text{CH}_2)_8-\text{SS}-(\text{CH}_2)_6-\text{OOC}-\text{C}=\text{CH}_2 \\   \\ \text{CH}_3 \end{array}$	325	338
19	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{COO}-(\text{CH}_2)_{10}-\text{SS}-(\text{CH}_2)_{10}-\text{OOC}-\text{C}=\text{CH}_2 \\   \\ \text{CH}_3 \end{array}$	332	347
20	$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C}-\text{S}-(\text{CH}_2)_{10}-\text{SS}-(\text{CH}_2)_{10}-\text{S}-\text{C}=\text{CH}_2 \\   \\ \text{H} \end{array}$	297	315
21	$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C}-\text{OOC}(\text{CH}_2)_{11}\text{SS}(\text{CH}_2)_{11}\text{OOC}-\text{C}=\text{CH}_2 \\   \\ \text{H} \end{array}$	271	293

5	22	$\text{H}_2\text{C}=\overset{\text{H}}{\underset{ }{\text{C}}}-\text{SOC}(\text{CH}_2)_7\text{SS}(\text{CH}_2)_7\text{COS}-\overset{\text{H}}{\underset{ }{\text{C}}}=\text{CH}_2$	310	340
10	23	$\text{H}_2\text{C}=\overset{\text{H}}{\underset{ }{\text{C}}}-\text{COO}(\text{CH}_2)_2\text{SS}(\text{CH}_2)_2\text{OOC}-\overset{\text{H}}{\underset{ }{\text{C}}}=\text{CH}_2$	335	343
15	24	$\text{H}_2\text{C}=\overset{\text{CH}_3}{\underset{ }{\text{C}}}-\text{CONH}(\text{CH}_2)_7\text{SS}(\text{CH}_2)_7\text{HNOC}-\overset{\text{CH}_3}{\underset{ }{\text{C}}}=\text{CH}_2$	324	342
20	25	$\text{H}_2\text{C}=\overset{\text{H}}{\underset{ }{\text{C}}}-\text{C}_6\text{H}_4-(\text{CH}_2)_6\text{SS}-(\text{CH}_2)_6\text{C}_6\text{H}_4-\overset{\text{H}}{\underset{ }{\text{C}}}=\text{CH}_2$	316	339
25	26	$\text{H}_2\text{C}=\overset{\text{CH}_3}{\underset{ }{\text{C}}}-\text{COO}-\text{CH}_2\text{CH}_2\text{O}-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}_2-\text{S}-\text{S}-\text{CH}_2\text{CH}_2\text{O}-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}_2-\text{OOC}-\overset{\text{CH}_3}{\underset{ }{\text{C}}}=\text{CH}_2$	340	333
30	27	$\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}=\text{CH}_2$	303	328

35 Examples 28 and 29 and Comparative Example 3

The compound used in Example 5 was dissolved in acetone to give a 1% solution. The solution was applied to "Cast Well" according to the same procedure as in Examples 1 to 13. One minute after application, the coated surface was washed with pure acetone. A stainless steel rod was bonded with "Panavia EX" (made by Kuraray Co., Ltd.) (Example 28)

Test pieces were prepared in the same manner as above using the compound used in Example 19. (Example 29)

For comparison, test pieces were prepared in the same manner as above, except that the acetone solution was not applied to "Cast Well".

(Comparative Example 3)

One hour after bonding, the test pieces were immersed in water at 37°C for 24 hours and then at 70°C for 10 days. The tensile bond strength was measured in the same manner as in Example 1 to 13. The average bond strength was 280 kg/cm<sup>2</sup> and 165 kg/cm<sup>2</sup> in Examples 28 and 29, respectively, whereas it was 31 kg/cm<sup>2</sup> in Comparative Example 3.

Examples 30 and 31 and Comparative Example 4

55 A two-part adhesive (paste type) of the following composition was prepared.

Paste A	
Bis-GMA	12.5 parts by weight
Triethyleneglycol dimethacrylate	12.5
Adhesive component in Example 5	0.1
N,N-diethanol-p-toluidine	0.5
Silane-treated quartz powder	74.5

Paste B	
Bis-GMA	12.5 parts by weight
Triethyleneglycol dimethacrylate	12.5
Benzoyl peroxide	0.5
Silane-treated quartz powder	74.5

Paste A and paste B were mixed in equal amount to give an adhesive. Using this adhesive, a sand-blasted stainless steel rod was bonded to dental gold alloy ("Herador H", Au : 79%, Pt : 10%, Pd : 8%, made by Heraus Edulmetale GmbH in West Germany) polished with silicon carbide abrasive paper (1000 grit). Bonding was performed in the same manner as in Examples 1 to 13 except that the primer was not applied.

The test piece was immersed in water at 37 °C for 24 hours, and the tensile bond strength was measured. Failure took place at the interface between the gold alloy and the adhesive, and the average value (of 8 measurements) was 234 kg/cm<sup>2</sup>. (Example 30)

The same procedure as mentioned above was repeated except that the adhesive component in Example 5 was replaced by the adhesive component in Example 19. The average strength was 201 kg/cm<sup>2</sup>. (Example 31)

For comparison, the same procedure as Examples 30 and 31 was repeated except that paste A was replaced by paste A' (in which the adhesive component in Example 5 was excluded). Failure took place at the interface between the gold alloy and the adhesive, and the average value was 106 kg/cm<sup>2</sup>. (Comparative Example 4)

#### Example 32

A two-part adhesive (powder-liquid mix type) of the following composition was prepared.

Powder component C	
Silane-treated silica powder	100.0 parts by weight
Sodium benzenesulfinate	0.4
N,N-diethanol-p-toluidine	0.5

Liquid component D	
Bis-GMA	50 parts by weight
1,6-hexanediol dimethacrylate	39
10-methacryloyloxydecyl dihydrogen phosphate	10
10-mercaptopdecyl methacrylate	1
Benzoyl peroxide	1

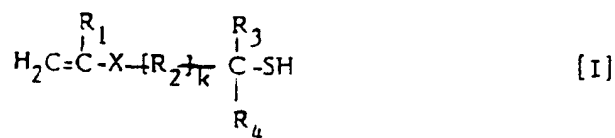
A paste adhesive was prepared by mixing the powder component C (3 g) and the liquid component D (1 g). Using this paste adhesive, a sand-blasted stainless steel rod was bonded to dental gold alloy "Herador H" polished with silicon carbide abrasive paper (1000 grit). Bonding was performed in the same manner as in Examples 1 to 13 except that the primer was not applied.

The test piece was immersed in water at 37 °C for 24 hours, and the tensile bond strength was measured. Cohesive Failure of the adhesive took place, and the average value (of 8 measurements) was

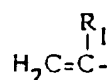
315 kg/cm<sup>2</sup>.

## Claims

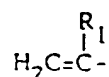
1. An adhesive comprising (a) a compound having at least one mercapto group or polysulfide group joined to a saturated carbon atom and at least one olefinic double bond and (b) a solvent that does not copolymerize with the said compound, in which the compound (a) has either the formula



where R<sub>1</sub> is a hydrogen atom or methyl group; R<sub>2</sub> is a C<sub>1-10</sub> organic group (which may contain a



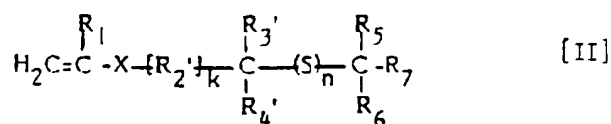
group and/or mercapto group); each of R<sub>3</sub> and R<sub>4</sub> is a C<sub>1-10</sub> organic group (which may contain a



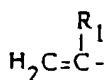
group and/or mercapto group); a hydrogen or halogen atom, or a mercapto group; or two or three of R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are optionally joined to each other to form a cyclic structure when R<sub>3</sub> and/or R<sub>4</sub> is an organic group; X denotes -COO-, -OOC-, -CONH-, -COS-, -SOC-, -S-, or



and k is 0 or 1, or the formula

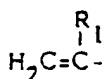


where R<sub>1</sub>, k and X are as defined above; R<sub>2</sub>' is a C<sub>1-10</sub> organic group (which may contain a



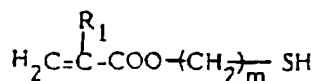
group and/or polysulfide group); each of R<sub>3</sub>', R<sub>4</sub>', R<sub>5</sub>, R<sub>6</sub> and R<sub>7</sub> is a C<sub>1-10</sub> organic group (which may

contain a



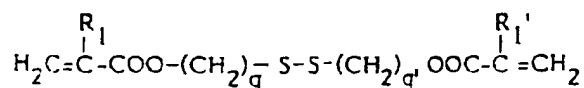
group and/or polysulfide group), a hydrogen or halogen atom, or a mercapto group; or two or three of  $R_2'$ ,  $R_3'$ , and  $R_4'$  are optionally joined to each other to form a cyclic structure when  $R_2'$  and/or  $R_4'$  is an organic group; and/or two or three of  $R_5$ ,  $R_6$ , and  $R_7$  are optionally joined to each other to form a cyclic structure when they are organic groups; and  $n$  denotes an integer of from 2 to 6.

2. An adhesive as claimed in Claim 1, in which the compound (a) has the formula



where  $R_1$  is as defined in Claim 1 and  $m$  is an integer of from 6 to 20.

3. An adhesive as claimed in Claim 1, in which the compound (a) has the formula



where  $R_1$  is as defined in Claim 1;  $R_1'$  is the same as  $R_1$ ; and each of  $q$  and  $q'$  is an integer of from 2 to 20.

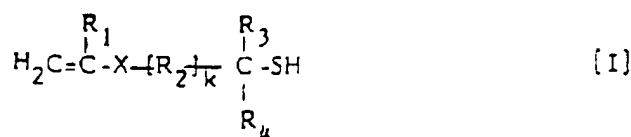
4. An adhesive as claimed in any one of Claims 1 to 3, in which the solvent is a volatile organic solvent, water, or a mixture thereof.
5. An adhesive as claimed in any one of Claims 1 to 4 comprising 0.0001 to 99 wt% of the compound (a) and 99.9999 to 1 wt% of the solvent.
6. An adhesive as claimed in any one of Claims 1 to 5 further comprising a polymerizable monomer that copolymerises with the compound (a).
7. An adhesive comprising (a) a compound having at least one mercapto group or polysulfide group joined to a saturated carbon atom and at least one olefinic double bond and (b) a polymerizable monomer copolymerizable with compound (a), compound (a) being as defined in Claim 1.
8. An adhesive as claimed in Claim 7, in which the compound (a) is as defined in Claim 2.
9. An adhesive as claimed in Claim 7, in which the compound (a) is as defined in Claim 3.
10. An adhesive as claimed in any one of Claims 7 to 9 in which the polymerizable monomer is a (meth)acrylate ester.
11. An adhesive as claimed in any one of Claims 7 to 10 comprising 0.005 to 99 wt% of the compound (a) and 99.995 to 1 wt% of the polymerizable monomer.



12. An adhesive as claimed in Claim 10 or 11 further comprising a volatile organic solvent and/or water.
13. An adhesive as claimed in any one of Claims 1 to 12, further comprising a polymerization initiator.
14. An adhesive as claimed in any one of Claims 1 to 13 further comprising a filler.
15. An adhesive as claimed in any preceding claim, for use in dental treatment.
16. Use of an adhesive as claimed in any one of Claims 1-14 for adhering metallic material under conditions where water resistance is required.
17. Use, as claimed in Claim 10, wherein the metallic material is a precious metal.

# Revendications

1. Un adhésif comprenant (a) un composé ayant au moins un groupe mercapto ou un groupe polysulfure uni à un atome de carbone saturé et au moins une double liaison oléfinique et (b) un solvant qui ne se copolymérise pas avec ledit composé, dans lequel le composé (a) a soit la formule



dans laquelle R<sub>1</sub> est un atome d'hydrogène ou un groupe méthyle ; R<sub>2</sub> est un groupe organique en C<sub>1-40</sub> (qui peut contenir un groupe



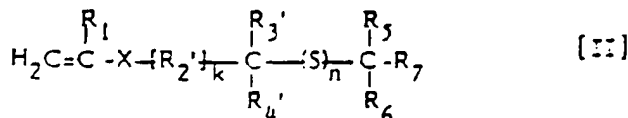
et/ou un groupe mercapto) ; chacun de R<sub>3</sub> et R<sub>4</sub> est un groupe organique en C<sub>1-40</sub> (qui peut contenir un groupe



et/ou un groupe mercapto), un atome d'hydrogène ou un atome d'halogène, ou un groupe mercapto ; ou deux ou trois de R<sub>2</sub>, R<sub>3</sub> et R<sub>4</sub> sont éventuellement unis entre eux pour former une structure cyclique lorsque R<sub>3</sub> et/ou R<sub>4</sub> est (sont) un groupe organique ; X représente -COO-, -OOC-, -CONH-, -COS-, -SOC-, -S- ou



et k est 0 ou 1, soit la formule



dans laquelle  $\text{R}_1$ ,  $k$  et  $\text{X}$  sont comme définis ci-dessus ;  $\text{R}_2'$  est un groupe organique en  $\text{C}_{1-40}$  (qui peut contenir un groupe

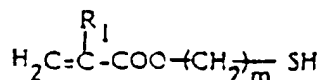


et/ou un groupe polysulfure) ; chacun de  $\text{R}_3'$ ,  $\text{R}_4'$ ,  $\text{R}_5$ ,  $\text{R}_6$  et  $\text{R}_7$  est un groupe organique en  $\text{C}_{1-40}$  (qui peut contenir un groupe



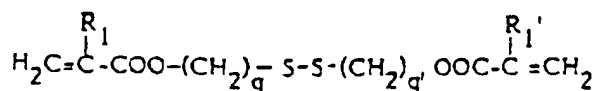
et/ou un groupe polysulfure), un atome d'hydrogène ou un atome d'halogène, ou un groupe mercapto ; ou deux ou trois de  $\text{R}_3'$ ,  $\text{R}_4'$  et  $\text{R}_4'$  sont facultativement unis entre eux pour former une structure cyclique lorsque  $\text{R}_3'$  et/ou  $\text{R}_4'$  est(sont) un groupe organique ; et/ou deux ou trois de  $\text{R}_5$ ,  $\text{R}_6$  et  $\text{R}_7$  sont facultativement unis entre eux pour former une structure cyclique lorsqu'ils sont des groupes organiques ; et  $n$  est un entier de 2 à 6.

2. Un adhésif selon la revendication 1, dans lequel le composé (a) a pour formule



dans laquelle  $\text{R}_1$  est comme défini dans la revendication 1 et  $m$  est un entier de 6 à 20.

3. Un adhésif selon la revendication 1, dans lequel le composé (a) a pour formule



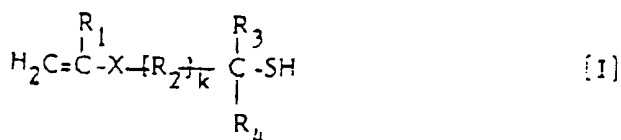
dans laquelle  $\text{R}_1$  est comme défini dans la revendication 1 ;  $\text{R}_1'$  est comme  $\text{R}_1$  ; et chacun de  $q$  et  $q'$  est un entier de 2 à 20.

4. Un adhésif selon l'une quelconque des revendications 1 à 3, dans lequel le solvant est un solvant organique volatil, l'eau ou un de leurs mélanges.
5. Un adhésif selon l'une quelconque des revendications 1 à 4 comprenant 0,0001 à 99 % en poids du composé (a) et 99,9999 à 1 % en poids du solvant.
6. Un adhésif selon l'une quelconque des revendications 1 à 5 comprenant de plus un monomère polymérisable qui se copolymérise avec le composé (a).

7. Un adhésif comprenant (a) un composé ayant au moins un groupe mercapto ou un groupe polysulfure uni à un atome de carbone saturé et au moins une double liaison oléfinique et (b) un monomère polymérisable copolymérisable avec le composé (a), le composé (a) étant comme défini dans la revendication 1.
8. Un adhésif selon la revendication 7, dans lequel le composé (a) est comme défini dans la revendication 2.
9. Un adhésif selon la revendication 7, dans lequel le composé (a) est comme défini dans la revendication 3.
10. Un adhésif selon l'une quelconque des revendications 7 à 9, dans lequel le monomère polymérisable est un ester (méth)acrylate.
11. Un adhésif selon l'une quelconque des revendications 7 à 10 comprenant 0,005 à 99 % en poids du composé (a) et 99,995 à 1 % en poids du monomère polymérisable.
12. Un adhésif selon la revendication 10 ou 11 comprenant de plus un solvant organique volatil et/ou de l'eau.
13. Un adhésif selon l'une quelconque des revendications 1 à 12 comprenant de plus un amorceur de polymérisation.
14. Un adhésif selon l'une quelconque des revendications 1 à 13 comprenant de plus une charge.
15. Un adhésif selon l'une quelconque des revendications précédentes pour l'emploi dans un traitement dentaire.
16. Utilisation d'un adhésif selon l'une quelconque des revendications 1 à 14 pour faire adhérer une matière métallique dans des conditions nécessitant la résistance à l'eau.
17. Utilisation selon la revendication 16, dans laquelle la matière métallique est un métal précieux.

#### Patentansprüche

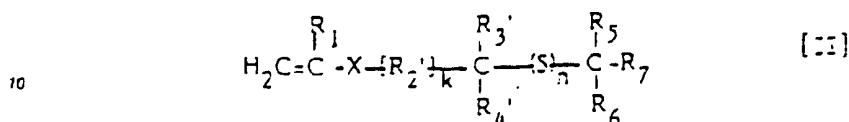
1. Klebstoff, welcher (a) eine Verbindung mit zumindest einer Mercapto-Gruppe oder Polysulfid-Gruppe, die an ein gesättigtes Kohlenstoffatom gebunden sind, und zumindest einer olefinischen Doppelbindung, und (b) ein Lösungsmittel, das mit genannter Verbindung nicht copolymerisiert, enthält, wobei die Verbindung (a) entweder die Formel



- besitzt,
- in der  $\text{R}_1$  ein Wasserstoffatom oder eine Methylgruppe darstellt;  $\text{R}_2$  eine  $\text{C}_1$ - $\text{C}_{10}$  organische Gruppe (die eine  $\text{H}_2\text{C}=\text{CR}_1$ -Gruppe und/oder eine Mercapto-Gruppe enthalten kann) darstellt;  $\text{R}_3$  und  $\text{R}_4$  jeweils eine  $\text{C}_1$ - $\text{C}_{10}$  organische Gruppe (die eine  $\text{H}_2\text{C}=\text{CR}_1$ -Gruppe und/oder Mercapto-Gruppe enthalten kann), ein Wasserstoff oder Halogen Atom, oder eine Mercapto-Gruppe darstellt; oder zwei oder drei der  $\text{R}_2$ -,  $\text{R}_3$ -, und  $\text{R}_4$ -Gruppen sind wahlweise miteinander verbunden um eine zyklische Struktur auszubilden, wenn  $\text{R}_3$  und/oder  $\text{R}_4$  eine organische Gruppe darstellt; X bezeichnet  $-\text{COO}-$ ,  $-\text{OOC}-$ ,  $-\text{CONH}-$ ,  $-\text{COS}-$ ,  $-\text{SOC}-$ ,  $-\text{S}-$ , oder

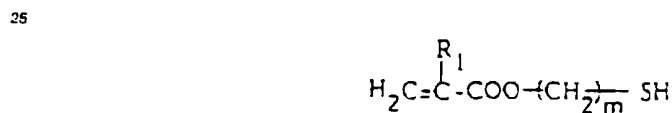


5 und k ist 0 oder 1, oder die Formel



15 worin  $\text{R}_1$ , k und X wie oben definiert sind;  $\text{R}_2'$  eine  $\text{C}_{1-40}$  organische Gruppe (welche eine  $\text{H}_2\text{C}=\text{GR}_1$ -Gruppe und/oder Polysulfid-Gruppe enthalten kann) darstellt; jede der Gruppen  $\text{R}_3'$ ,  $\text{R}_4'$ ,  $\text{R}_5$ ,  $\text{R}_6$  und  $\text{R}_7$  eine  $\text{C}_{1-40}$  organische Gruppe (welche eine  $\text{H}_2\text{C}=\text{CR}_1$ -Gruppe und/oder eine Polysulfid-Gruppe enthalten kann), ein Wasserstoff oder ein Halogen Atom, oder eine Mercapto-Gruppe darstellt; oder zwei oder drei der  $\text{R}_2'$ ,  $\text{R}_3'$  und  $\text{R}_4'$ -Gruppen wahlweise unter Bildung einer zyklischen Struktur miteinander verbunden sind, wenn  $\text{R}_3'$  und/oder  $\text{R}_4'$  eine organische Gruppe darstellen; und/oder zwei oder drei der  $\text{R}_5$ ,  $\text{R}_6$  und  $\text{R}_7$ -Gruppen wahlweise mit einander verbunden sind, um eine zyklische Struktur zu bilden, wenn sie organische Gruppen darstellen; und n eine ganze Zahl von 2 bis 6 ist.

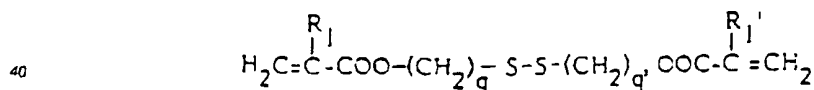
2. Klebstoff gemäß Anspruch 1, in welchem Verbindung (a) die Formel



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besitzt,  
in der  $\text{R}_1$  wie in Anspruch 1 definiert ist und m eine ganze Zahl von 6 bis 20 ist.

35 3. Klebstoff gemäß Anspruch 1, in welchem Verbindung (a) die Formel



45 besitzt,  
in der  $\text{R}_1$  wie in Anspruch 1 definiert ist;  $\text{R}_1'$  identisch ist mit  $\text{R}_1$ ; und q und q' jeweils eine ganze Zahl von 2 bis 20 darstellen.

4. Klebstoff gemäß einem der Ansprüche 1 bis 3, in welchem das Lösungsmittel ein flüchtiges organisches Lösungsmittel, Wasser oder eine Mischung derselben ist.

50 5. Klebstoff gemäß einem der Ansprüche 1 bis 4, welcher 0.0001 bis 99 Gewichtsprozent der Verbindung (a) und 99.9999 bis 1 Gewichtsprozent des Lösungsmittels enthält.

6. Klebstoff gemäß einem der Ansprüche 1 bis 5, welcher weiterhin ein polymerisierbares Monomer, das mit Verbindung (a) copolymerisiert, enthält.

7. Klebstoff, welcher (a) eine Verbindung mit zumindest einer Mercapto- oder Polysulfid-Gruppe, die an ein gesättigtes Kohlenstoffatom gebunden sind und zumindest eine olefinische Doppelbindung und (b)

ein polymerisierbares Monomer, das mit der gemäß Anspruch 1 definierten Verbindung (a) copolymerisierbar ist, enthält.

8. Klebstoff gemäß Anspruch 7, in welchem Verbindung (a) gemäß Anspruch 2 definiert ist.
9. Klebstoff gemäß Anspruch 7, in welchem Verbindung (a) gemäß Anspruch 3 definiert ist.
10. Klebstoff gemäß einem der Ansprüche 7 bis 9, in welchem das polymerisierbare Monomer ein (Meth)acrylat-Ester ist.
11. Klebstoff gemäß einem der Ansprüche 7 bis 10, welcher 0.005 bis 99 Gewichtsprozent der Verbindung (a) und 99.995 bis 1 Gewichtsprozent des polymerisierbaren Monomers enthält.
12. Klebstoff gemäß Anspruch 10 oder 11, welcher zusätzlich ein flüchtiges organisches Lösungsmittel und/oder Wasser enthält.
13. Klebstoff gemäß einem der Ansprüche 1 bis 12, welcher zusätzlich einen Starter für die Polymerisation enthält.
14. Klebstoff gemäß einem der Ansprüche 1 bis 13, welcher zusätzlich einem Füllstoff enthält.
15. Klebstoff gemäß einem der vorstehenden Ansprüche zur Benutzung in zahnärztlicher Behandlung.
16. Verwendung des Klebstoffes gemäß einem der Ansprüche 1 bis 14 zum Ankleben eines metallischen Materials unter Bedingungen bei denen Beständigkeit gegen Wasser notwendig ist.
17. Verwendung gemäß Anspruch 16, wobei das metallische Material ein Edelmetall ist.